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ELECTROCHEMICAL BEHAVIOR OF A  
PALLADIUM HYDROGEN DIFFUSION ELECTRODE

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# ABSTRACT

✓  
Electrochemical studies on palladium hydrogen diffusion electrodes indicate that sufficiently high current densities can be achieved <sup>making</sup> ~~to make~~ their use as ~~fuel cell~~ hydrogen electrodes ~~in fuel cell applications~~ practically feasible. Using a palladium oxide catalyst, formed by heating the electrode in air at 600°C, maximum current densities of 75 <sup>50</sup> ma/cm<sup>2</sup> at a solution temperature of 24°C and 140 <sup>50</sup> ma/cm<sup>2</sup> at 43.5°C were achieved.

The ability of hydrogen to pass freely through thin palladium foils presents the interesting possibility of using palladium diffusion membranes as hydrogen electrodes in fuel cell applications. The results of preliminary studies on the electrochemical behavior of palladium hydrogen diffusion electrodes indicate that, with suitable pretreatment, sufficiently high current densities can be achieved to make such applications practically feasible.

Potentiostatic anodic polarization curves were made using (1) apparatus and techniques described elsewhere. The palladium electrodes were tubes with a wall thickness of .01 inch and presented a surface area of 10 cm<sup>2</sup> to the solution when mounted. The special electrode mount employed is described in Figure 1. (2) Polarization flasks were identical to those used previously. Nitrogen was continuously bubbled through the solution, which was 1N sulfuric acid prepared from reagent grade acid and triply distilled water. Hydrogen was admitted to the inside of the electrode at pressures from 0 to 10 psia. Electrodes were initially prepared by abrading with 2/0 emery paper, ultrasonic washing in detergent, and rinsing in triply distilled water. Potentials were measured versus a saturated calomel electrode through a Luggin probe salt bridge. Currents

were taken after 3 minutes at each potential by measuring the voltage drop across a precision resistor or by a precision ammeter. Unless otherwise noted, measurements were made at room temperature ( $24^{\circ}\text{C} \pm 1^{\circ}$ ).

In solution, the palladium electrode was found to maintain a potential of +50 mv vs. hydrogen for a period of several hours after the admittance of hydrogen, after which the potential slowly drifted to the reversible hydrogen potential. Anodic polarization measurements were made with the electrode initially at +50 mv vs. hydrogen, and at the hydrogen potential. For simplicity of presentation, the results of polarization measurements will be reported in terms of the maximum current densities achieved. Although some variation in time dependence was noted, the maximum current density obtained was approximately  $10 \text{ ma/cm}^2$  for either starting potential.

No change in the maximum current density was noted on increasing the hydrogen pressure inside the electrode from 0 to 10 psia. This leads to the conclusion that the controlling step is pressure insensitive. In contrast, increases in the solution temperature produced corresponding increases in the maximum current. At a solution temperature of  $90^{\circ}\text{C}$ , the maximum current was increased to  $27 \text{ ma/cm}^2$ . The effects of pretreatment and solution temperature on performance are shown in Table I.

A decided improvement in performance was obtained by heating the electrodes in air at temperatures above 450°C before immersion in the solution. A prior heat treatment for one hour at 600°C increased the maximum current density to 75 ma/cm<sup>2</sup> at a solution temperature of 24°C, and to 140 ma/cm<sup>2</sup> at 43.5°C. Similar heat treatment in an argon atmosphere instead of air produced no increase in maximum current density. This leads to the conclusion that palladium oxide itself acts as a quite efficient catalyst for the reaction.

In order to determine more precisely the site of the catalytic activity, the outside surface of an electrode was abraded with 2/0 emery paper after heat treatment. Removal of the oxide from the outside surface produced no appreciable decrease in the maximum current density. However, when both the inside and outside electrode surfaces were similarly abraded, the maximum current density was decreased to 32 ma/cm<sup>2</sup> indicating that the controlling step occurs on the gas rather than the electrolyte side of the electrode.

A less significant increase in performance was obtained by platinizing both walls of an electrode after heating in argon. In this case, the maximum current density was 20 ma/cm<sup>2</sup>. Platinized platinum thus appears to be a much less efficient catalyst than the oxide itself. However, using a uranium



(3)  
hydride catalyst, Küssner and Wicke have measured the consumption of hydrogen on the gas side of a palladium membrane electrode during anodic polarization, and found a maximum hydrogen flow equivalent to  $70 \text{ ma/cm}^2$ .

Further investigations on the behavior of the palladium hydrogen diffusion electrode are now in progress, including the effects of wall thickness, solution composition, pretreatment, and various other catalysts.

## ACKNOWLEDGMENTS

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References:

1. S. J. Acello and N. D. Greene, Corrosion, 18, 286t (1962)
2. N. D. Greene, Corrosion, 15, 369t (1959)
3. A. Küssner and E. Wicke, Zeitschrift fur Physikalische Chemie (Neue Folge) 24, 152 (1960)

TABLE I

Pretreatment	Solution Temp. °C	Maximum Current Density (ma/cm <sup>2</sup> )
None	24	10
None	60	18
None	90	27
Heated 1 hr. in air at 600°C	24	75
" " "	43.5	140
Heated 1 hr. in argon at 600°C	24	6.9
Both walls Platinized	24	20

Figure Titles

Figure 1. Cross-sectional drawing of special mount  
for palladium hydrogen diffusion electrode.

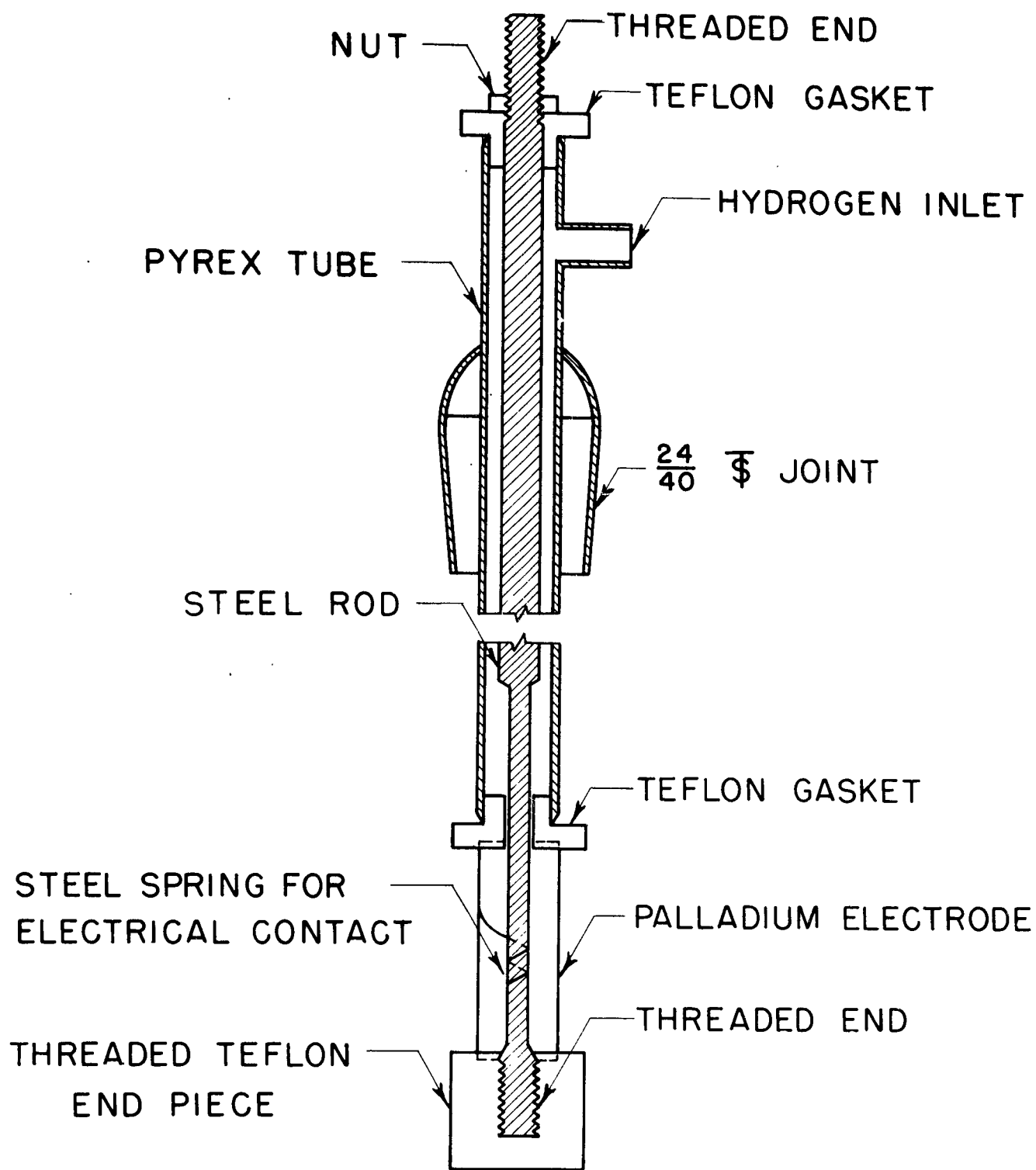


FIGURE I

ERRATA TO  
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This Figure replaces Figure 1 in the original report, which is an earlier, less successful version of the electrode mount.



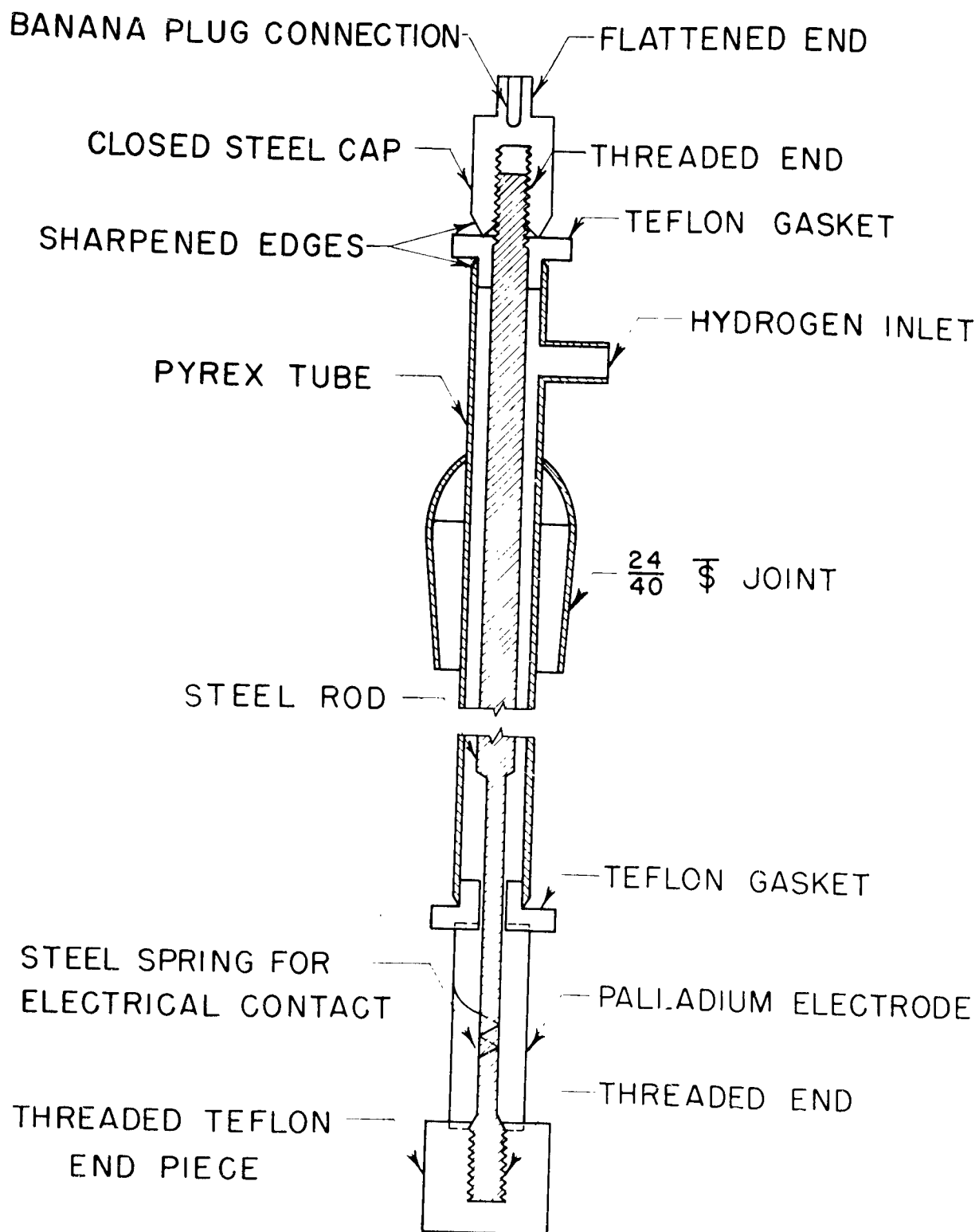


FIGURE I